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(NASA-CR-155038) ATOM-RADICAL REACTION SYSTEMS Final Report (Michigan Univ.) 12 p HC A02/MF A01 CSCL 04A

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ATOM-RADICAL REACTION SYSTEMS

FINAL TECHNICAL REPORT

Prepared on behalf of the project by

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under contract with:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
JOHNSON SPACE CENTER
GRANT NO. NSG-9031
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This report summarizes the results of the effort under NASA Grant NSG 9031. The subject grant provided support for the study of atom-radical reaction systems in order to develop techniques which could be used to carry out in situ measurements of specie densities in the upper atmosphere. The results of these efforts are discussed in this report.

The detailed understanding of stratospheric photochemistry had long been hampered by the inability to perform in situ measurements of the reactive species which dominated the atmospheric chemistry. This situation was changed dramatically with our development of the Laminar Flow Through-Resonance Fluorescence technique which permitted the direct measurement of absolute density for most atomic and diatomic constituents. This system is shown schematically in Figures 1 through 3 and its use in determining $O(^3P)$ and OH densities is described in Appendices A and B.

In addition to atomic and diatomic species which can generally be observed directly, there are numerous stratospheric constituents which are not amenable to direct resonance fluorescence detection. They fall into two closely related categories. The first are the diatomics such as ClO and BrO which cannot be observed by fluorescence due to predissociation of the upper electronic state. The second category contains the polyatomics such as H_2O, NO_2, HO_2 and CH_4 which cannot be observed due to the complexity and diffuseness of their spectra, the typical situation for a molecule with 3 or more atoms. To measure densities of these species, it is necessary to convert them to a form which can be observed directly by fluorescence. This conversion can be accomplished either chemically or photolytically. Both techniques were used here in a laboratory system so that they can be used in the flight program.

The system used is shown in Figure 4. It is a rather typical one inch flow reactor which is widely used in the study of gas phase kinetics. The species of interest can be generated directly in the upstream discharge or indirectly by adding another gas through the loop injector.

The sliding injector is used to add other reactant species to the ones already present at varying distances upstream of the detection cells. The multiple fluorescence cell shown provides the capability of simultaneously monitoring several species. Appropriate resonance lamps mounted in microwave or RF discharge cavities atop the cells illuminate the flowing gas and the resultant emission can be detected by a variety of filter-and-phototube and/or spectrometer-and-phototube arrangements mounted perpendicular to the illumination direction.

In addition to the obvious capability to determine the effects of added chemical components in the flow tube, this system can also compare the performance of various lamp designs; e.g., flowing versus static and microwave versus RF excitation. As a result of mircowave versus RF comparisons, both OH and Cl/ClO flight instruments used the microwave excitation due to its greatly enhanced intensity. It should be noted, however, that a serious program is underway in this laboratory to develop improved high power RF oscillators.

Flow rates were measured using either a mass flow controller or the standard volume - dP/dt method. Pressures were measured with variable reluctance pressure transducers. Pumping was achieved with 2 Welch Duo Seal 1397B mechanical pumps or a high capacity Roots blower/forepump combination. Velocities in excess of 12000 cm/sec were attainable at 1-10 torr pressures.

The initial chemical conversion plan was to convert ClO to Cl by addition of O atoms:

$$ClO + O \rightarrow Cl + O_2.$$

This is also applicable to the conversion of BrO to Br, NO_2 to NO, and HO_2 to OH and, subsequently, H. Following conversion, which would be complete within a few cm due to the rapidity of the reactions, the resultant atom or diatomic could be detected by resonance fluorescence.

One of the difficulties in this approach is that we are adding O at densities near 10^{14} cm^{-3} to convert species at densities of 10^{7} cm^{-3}. In the case where atoms are produced in the conversion, the subsequent fluorescence detection is hampered by the large numbers of O atoms which can also fluoresce if there is any residual oxygen emission from the resonance lamp. The required seven orders of magnitude discrimination against O emission is attainable and should be done shortly.

For the present, however, the primary emphasis was on ClO conversion and, for this, an alternate method was used:

$$ClO + NO \rightarrow Cl + NO_2.$$

Not only does the NO addition avoid the interference from O, it also greatly simplifies the flight instrument package as it involves the addition of a stable gas rather than the complex process of adding atoms generated in another microwave discharge.

To verify that there were no interactions between NO and other atmospheric constituents which would give rise to spurious signals, the compatibility of NO with a variety of gases was checked. These other constituents included O_3, H_2, N_2, O_2, H_2O, HCl, CH_4, N_2O, Cl_2 and CO. There was no evidence of any signal enhancement due to interactions of NO with the aforementioned species. Furthermore, even at NO densities an order of magnitude greater than used in flight and with a lamp operating under extreme conditions, it was not possible to generate spurious signals comparable to those that the ClO → Cl conversion would give.

The companion experiment to the ClO measurement is the measurement of atomic Cl densities. In this case, a gas must be added to remove Cl so that background signals can be measured. The planned addition of NOCl was investigated and showed that NOCl generated fluorescent signals approximately two orders of magnitude greater than the real Cl signal would be. This necessitated finding a substitute.

Although HBr was acceptable from the standpoint of removing all Cl and not generating anomalous signals it is extremely corrosive and difficult to handle. Further investigation led to the selection of ethane since it fulfilled all criteria excellently: (1) removed all Cl; (2) did not generate spurious signals; (3) was easy to handle.

Work was also carried out on the O_2 filters used to filter the oxygen 1302 Å and the chlorine 1347 Å radiation out of the lamp beam and only pass the Cl 1188 Å line. Sealed filters were initially used but were found to deteriorate severely in performance due to formation of O_3 within the sealed unit. The solution was to flow O_2 through the filter so as to continuously replenish it and flush out the O_3 formed.

As was mentioned earlier, chemical conversion is only one technique; the other is photolytic conversion. This second method was developed for H_2O and can also be termed "fragment fluorescence." Suitable wavelength radiation (Lyman alpha at 1216 Å) is used to photolyze H_2O vapor, forming OH, some of which is in the electronically excited $A^2\Sigma^+$ state and can radiate at 3090 Å:

$$H_2O + Ly\ \alpha \rightarrow H + OH^* \quad (A)$$

$$OH^*(A) \rightarrow OH\ (X) + h\nu\ (3090\ Å).$$

Optimum signals are obtained with a highly reversed Lyman alpha lamp without any filters on the lamp side. Our studies have shown that this system has a detection sensitivity comparable to that for OH resonance fluorescence. This indicates that the flight instrument should be capable of operating at H_2O densities down to 10^7 or 10^8 cm^{-3}. Since stratospheric H_2O densities are in the 10^{11} to 10^{12} cm^{-3} range, there is more than sufficient capability to perform the experiment.

The work on the ClO and H_2O systems has proven extremely valuable to the overall experimental flight program and emphasizes the importance of the supporting laboratory system. Further and more complex work is presently underway to develop not only new techniques and capabilities but to improve our kinetic understanding of the various chemical systems.

FIGURE LEGENDS

Figure 1 Schematic of flight instrument along flow (descent) axis

Figure 2 Schematic of flight instrument in optical phane

Figure 3 Schematic of payload calibration system

Figure 4 Schematic of laboratory apparatus for studying atom-radical reaction systems

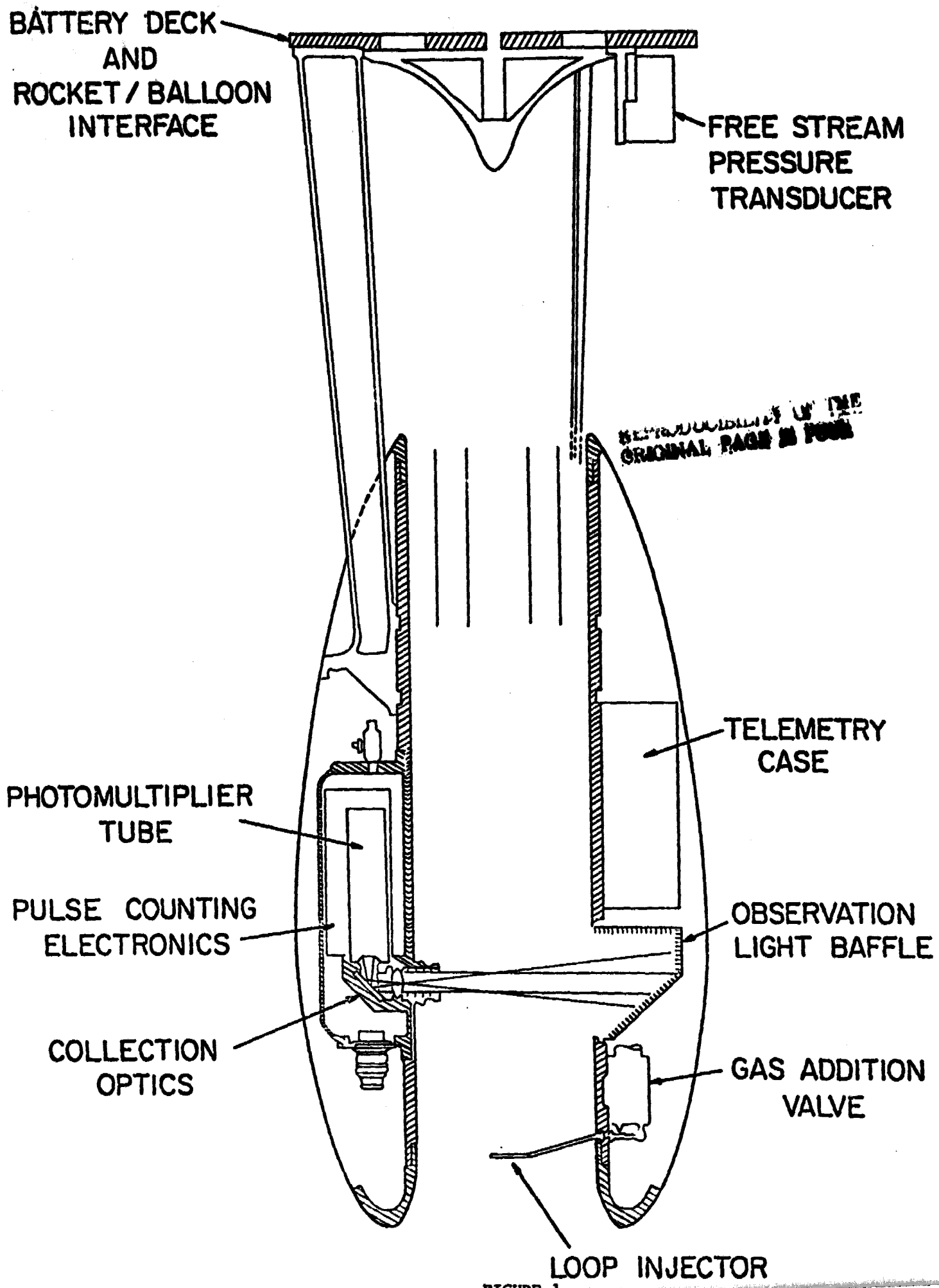
BATTERY DECK AND ROCKET / BALLOON INTERFACE
FREE STREAM PRESSURE TRANSDUCER
TELEMETRY CASE
PHOTOMULTIPLIER TUBE
PULSE COUNTING ELECTRONICS
OBSERVATION LIGHT BAFFLE
COLLECTION OPTICS
GAS ADDITION VALVE
LOOP INJECTOR

FIGURE 1

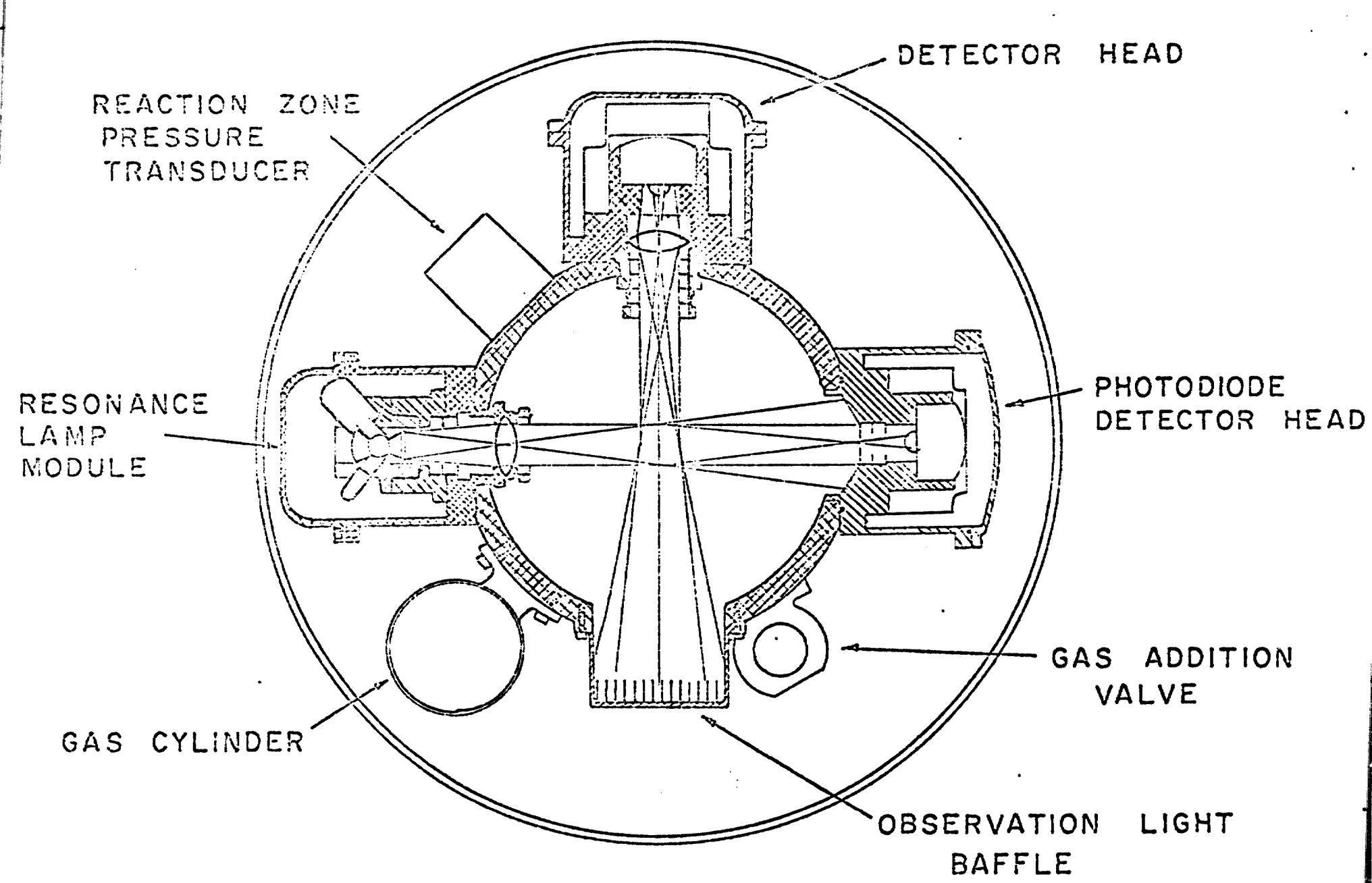
DETECTOR HEAD
REACTION ZONE PRESSURE TRANSDUCER
RESONANCE LAMP MODULE
PHOTODIODE DETECTOR HEAD
GAS ADDITION VALVE
GAS CYLINDER
OBSERVATION LIGHT BAFFLE

FIGURE 2

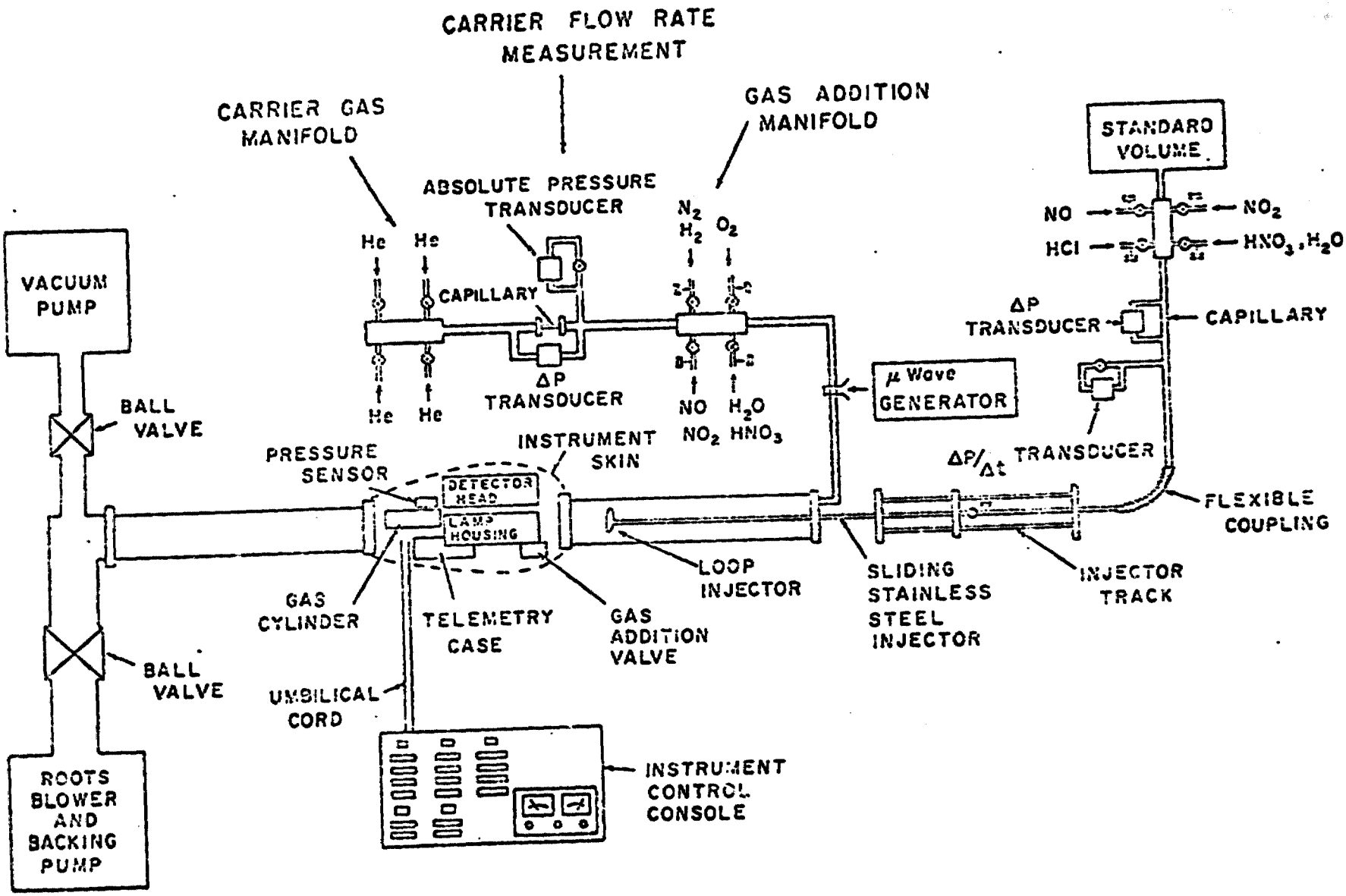
CARRIER FLOW RATE MEASUREMENT
CARRIER GAS MANIFOLD
GAS ADDITION MANIFOLD
ABSOLUTE PRESSURE TRANSDUCER
STANDARD VOLUME
VACUUM PUMP
He
He
CAPILLARY
N_2
H_2
O_2
NO
NO_2
HCl
HNO_3, H_2O
ΔP TRANSDUCER
CAPILLARY
ΔP TRANSDUCER
μ Wave GENERATOR
BALL VALVE
PRESSURE SENSOR
INSTRUMENT SKIN
DETECTOR HEAD
LAMP HOUSING
$\Delta P/\Delta t$ TRANSDUCER
FLEXIBLE COUPLING
GAS CYLINDER
TELEMETRY CASE
GAS ADDITION VALVE
LOOP INJECTOR
SLIDING STAINLESS STEEL INJECTOR
INJECTOR TRACK
BALL VALVE
UMBILICAL CORD
ROOTS BLOWER AND BACKING PUMP
INSTRUMENT CONTROL CONSOLE

FIGURE 3

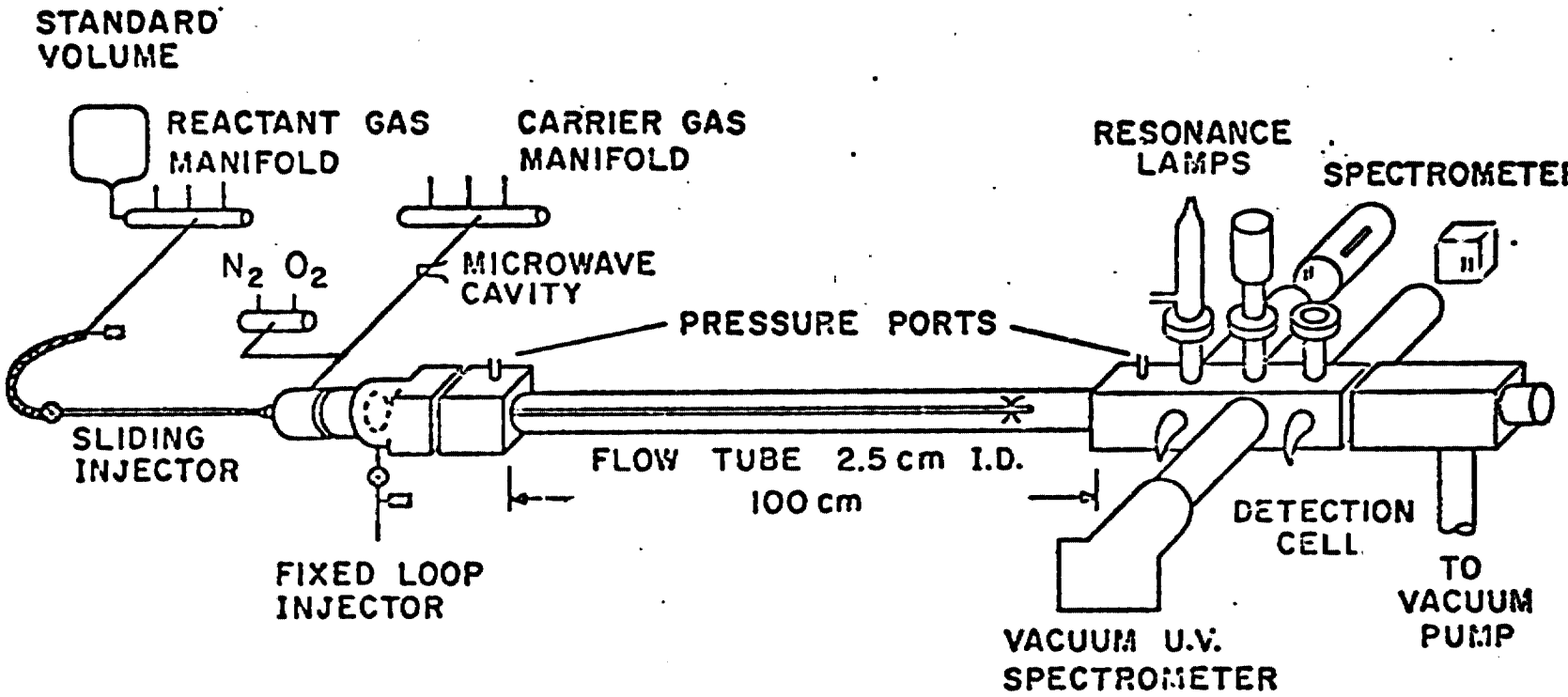
STANDARD VOLUME
REACTANT GAS MANIFOLD
CARRIER GAS MANIFOLD
RESONANCE LAMPS
SPECTROMETERS
N_2 O_2
MICROWAVE CAVITY
PRESSURE PORTS
SLIDING INJECTOR
FLOW TUBE 2.5 cm I.D.
100 cm
DETECTION CELL
FIXED LOOP INJECTOR
TO VACUUM PUMP
VACUUM U.V. SPECTROMETER

FIGURE 4